ADDITION REACTIONS TO &-CYCLOPROPYLIDENE KETONES AND ALDEHYDES.

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Abstract. ≪-Cyclopropylidene ketones show high reactivity towards 1,4-addition reactions.

 \propto -Cyclopropylidene aldehydes $\underline{1}$, aliphatic and aromatic \propto -cyclopropylidene ketones $\underline{2}$ and \propto -cyclopropylidene cycloalkanones $\underline{3}$, still unknown in 1977, are now easily available either by photooxygenation of enol ethers of cyclopropyl ketones, followed by PPh $_3$ reduction ($\underline{1}$) (1) or, better, by Wittig reaction of cyclopropylidenetriphenylphosphorane with \propto -keto- or \propto -aldoacetals followed by desacetalisation with moist silicagel (1, 2a-c, 3) (2).

Some ketones (e.g. 2d-g) are more easily obtained by the reaction of aldehydes \underline{l} with Grignard reagents (which leads exclusively to the 1,2 addition product), followed by oxidation with active MnO $_2$ (3).

H OH OH
$$R^2 MgX$$

2) Hydrolysis

R1

 R^2
 R^2

Examples $\frac{1a}{\underline{d}} \qquad \qquad 88\%^1 \quad R^1 = Me \quad R^2 = Ph \qquad \underline{2d} \quad 81\%^1$ $\frac{d}{\underline{d}} \qquad \qquad 62\%^1 \quad R^1 = R^2 = cyclopropyl \qquad \underline{g} \quad 50\%^1$ 1 yield of isolated product

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Reactions of ketones $\underline{2}$ and $\underline{3}$ with <u>organometallic reagents</u> give more or less expected results (scheme 1): thus methyl lithium leads exclusively to the 1,2 addition product, the $\not\sim$ -cyclopropylidene alcohol, lithium dimethylcuprate leads to the 1,4 addition product, the $\not\sim$ -cyclopropyl ketone, and Grignard reagents to a mixture of 1,2 and 1,4 addition products.

Scheme I. Addition of organometallic reagents to &-cyclopropylidene ketones.

It is interesting to compare these results with those observed for the corresponding α -isopropylidene ketones (table 1). For instance when treated with Me₂CuLi, 3,4-dimethyl 3-penten 2-one $\underline{4}$ gives the 1,4 addition product in low yield only, while the corresponding α -cyclopropylidene ketone $\underline{2b}$ gives the same kind of product in higher yield. In the same way mesityl oxide $\underline{5}$ gives the 1,2 addition product only when treated with MeMgI, whereas the ketone $\underline{2a}$ gives a mixture of the 1,2 and 1,4 addition products. Such differences are probably due to a relief of strain in the small ring of the cyclopropylidene system during 1,4 additions. The same tendency is also seen if the polarographic reduction potentials (4) of ketones $\underline{4}$ and $\underline{2b}$ are compared (see table I).

The reduction of \angle -cyclopropylidene ketones with <u>metal hydrides</u> was also studied. For instance, with LiAlH $_4$ (1 equivalent) cyclopropylidene-acetophenone 2c gives a mixture of the alcohol $\underline{6}$ and the ketone $\underline{7}$ ($\underline{6/7}$ = 30/70). With NaBH, in

$$\begin{array}{c|c} & & & \\ & & & \\ \hline & & & \\ & & & \\ \hline & & \\ \hline & & & \\ \hline & &$$

Reactions

Results after hydrolysis

21% 1,4 addition product72% enolisation (recovered enone) (4)

67% 1,4 addition product (the sole isolated product)

61% 1,2 addition product (5) (the sole isolated product)

1,2/1,4 addition products = 75/25 (sum of yields 60%)

- \underline{a} Polarographic reduction potential (6) -2.30 V (litt. -2.35 V (4))
- b Polarographic reduction potential (6) -2.00 V.

Table I. - 1,2 and 1,4 addition reactions of Me $_2$ CuLi and MeMgI with \propto -isopropylidene and \propto -cyclopropylidene ketones.

MeOH (2 equivalents) the same ketone gives the alcohol $\underline{8}$ only (77% yield of isolated product). Interestingly NaBH₄-CeCl₃ in MeOH (7) (1 equivalent) yields only the 1,2 addition product $\underline{6}$ (90% yield of isolated product); similar results are obtained with other α -cyclopropylidene ketones (see the following communication (8)).

 α -Cyclopropylidene ketones quickly add MeOH, H₂O and HCl. For example at 25°, in MeOH containing 0,5% KOH (w/v) cyclopropylidene-acetone 2a was instantaneously transformed into the β -methoxy-cyclopropylacetone 9a (69% yield of isolated product); mesityl oxide reacts much more slowly: $7 \, \text{h}$ at $25 \, \text{°}$ were necessary

to obtain a 70% conversion into $\underline{10a}$. Addition of water (5.5% COOH-COOH, $\underline{H_2O}$, DMSO at 25°) is also slower to $\underline{5}$ than to $\underline{2a}$: 10 h are required to obtain an only 30% conversion of $\underline{5}$ into $\underline{10b}$ while the complete desappearance of $\underline{2a}$ only needs 3 h (yield

of isolated $\underline{9b}$: 65%). 3-Cyclopropylidene 2-butanone $\underline{2b}$ instantaneously adds HCl (in CCl $_4$ at 25°) and yields 3-(1'-chloro cyclopropyl)2-butanone $\underline{11}$, (87% yield of isolated product).

BrOH addition (with NBS, DMSO, $\rm H_2O$ - the reaction starts with the attack of the double bond by a bromonium ion (9)) to α -cyclopropylidene ketones is also interesting. 3,4-Dimethyl 3-penten 2-one 4 gives the expected result: the sole isolated product is the β -hydroxy α -bromo ketone 13 (66% yield). The opposite is true for the α -cyclopropylidene ketone 2b: the only isolated product (47% yield) is the α -hydroxy β -bromo ketone 12 beside resinous compounds.

These analogies and differences between α -cyclopropylidene ketones and regular α -enones can be used to advantage in synthetic work : some applications are in progress (8).

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